

---

## **PRELIMINARY TRIALS ON THE EFFECT OF THIRD COMPONENTS IN HYDROCARBON-TYPE HYDRATE TESTS**

**ERNEST L. LIPPERT, JR., HAROLD A. PALMER, and FORREST F. BLANKENSHIP, University of Oklahoma, Norman**

Hydrocarbon-type hydrates of liquids give rise to fairly complicated binary systems, the phase behavior of which has only recently been completely elucidated from a schematic standpoint (11). The presence of a third component introduces a multiplicity of possible cases for almost none of which can a complete schematic picture of the phase behavior be outlined. Further progress in this connection has been slowed by the paucity of experimental data. This paper summarizes some accumulated information on the experimental behavior of ternary systems as gathered from a variety of investigations on hydrocarbon-type hydrates at the University of Oklahoma. Throughout this paper, the term hydrate will refer to "hydrocarbon-type hydrate," unless otherwise specified.

Aside from the theoretical interest, the effect of third components on hydrate equilibria has much practical significance in connection with separation and fractionation based on hydrate formation, the formation of hydrates from mixtures, the inhibition or avoidance of hydrate formation,

and the use of hydrate formation as a criterion of purity. Outside the laboratory, hydrates are rarely encountered except in the presence of one or more additional components and even in the laboratory small amounts of impurities are usually present.

Third components which are liquids or solids and their effect on hydrates of liquids at atmospheric pressure will be discussed first. The following classification of such third components is convenient.

- A. Non-hydrate formers, including molecules that are too large or too soluble in water;
- B. Hydrate formers, including only those molecules known to form hydrates stable at 1 atmosphere in the neighborhood of 0°C.; and
- C. Potential hydrate formers, including molecules known to form hydrates stable at pressures greater than one atmosphere, and also borderline cases for which the application of the limitations mentioned above under A are not definitely known.

Results from cases under each category will be discussed.

1. *The third component is of type A and is a liquid soluble in both aqueous and non-aqueous components.*

Sampson (7) studied the effect of ethyl alcohol on a sample of chloroform hydrate prepared from 300 ml. of distilled water and 25 ml. of chloroform. Alcohol was added to the sample in 1 ml. increments, and the equilibrium temperature determined after each addition. A decrease in temperature of about 0.1°C per ml. of alcohol prevailed from 3 ml. to 14 ml. of alcohol added. Slightly larger decreases were found for the first few ml. added; the first ml. caused a temperature drop of 0.14°C, and diminished decreases were observed toward the end of the trial when most of the hydrate had decomposed. These results are shown in Fig. 1.

Lippert (3) continued such studies under essentially identical conditions using isopropyl alcohol and, more recently, acetone. The results for acetone are typical. They are summarized in Table I and Fig. 2.

Average temperature drops obtained during comparable stages of the trials, when converted to a mole basis, gave the results shown in Table II.

**TABLE I**  
*Decomposition Temperature of Chloroform Hydrate on Addition of Acetone*

ML.	MOLES	$\Delta M$	°C	$\Delta^\circ C$	$\Delta^\circ C/\Delta M$
0			1.68		
1	0.0140	0.014	1.53	0.15	10.71
2	0.0280	0.014	1.39	0.14	10.00
3	0.0420	0.014	1.26	0.13	9.28
4	0.0560	0.014	1.14	0.12	8.57
5	0.0699	0.0139	1.03	0.11	7.91
6	0.0839	0.014	0.92	0.11	7.86
7	0.0979	0.014	0.83	0.09	6.43
8	0.112	0.0141	0.73	0.10	7.09
9	0.126	0.014	0.65	0.08	5.71
10	0.140	0.014	0.57	0.08	5.71
11	0.154	0.014	0.49	0.08	5.71
12	0.168	0.014	0.42	0.07	5.00

**TABLE II**  
*Average Temperature Drops*

THIRD COMPONENT	$-\Delta T$ PER MOLE OF THIRD COMPONENT
Ethyl alcohol	6.7°C
Isopropyl alcohol	7.5°C
Acetone	8.7°C

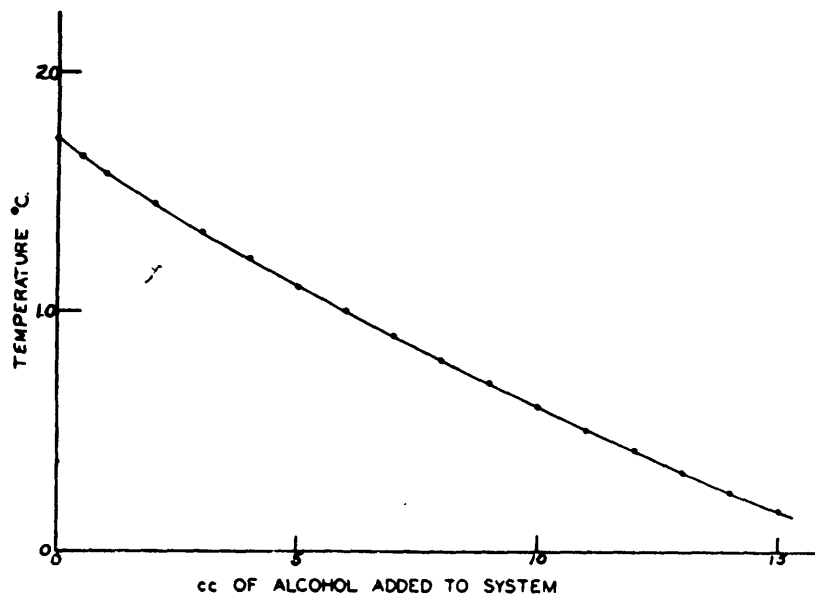


FIGURE 1. *Decomposition Temperature of Chloroform Hydrate on Addition of Ethyl Alcohol*  
Hydrate Formed from 300cc Water and 25cc Chloroform

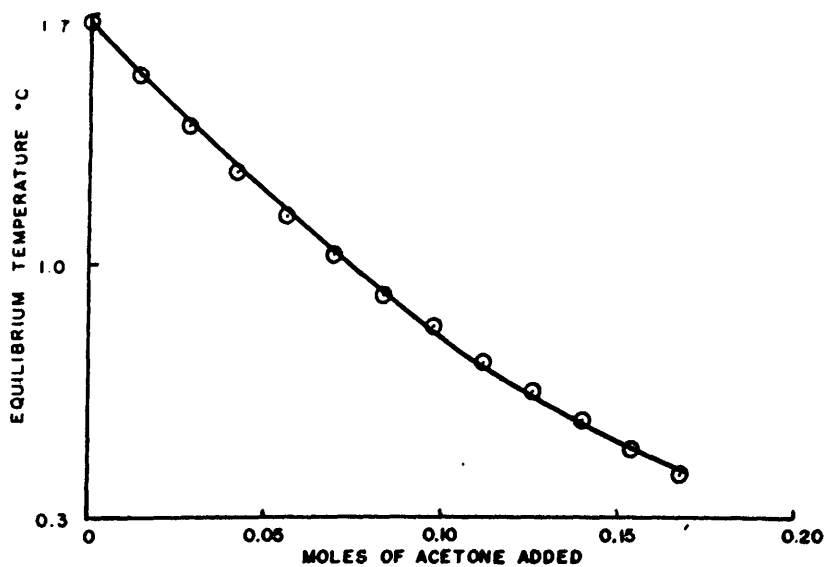


FIGURE 2. *Decomposition Temperatures of Chloroform Hydrate on Addition of Acetone*

Only qualitative conclusions can be drawn from the results because the compositions of the equilibrium liquids were not known.

*2. The third component is of type A and is soluble in only one of the other components.*

Slater (8) ascertained that sodium or potassium chlorides were not carried down in hydrate crystals, nor was there any adsorption of the electrolyte on forming crystals in salt solutions. This conclusion was further verified by Whalen (11), who found that the molal decomposition temperature depressions due to toluene were  $-0.72^{\circ}\text{C}$  for chloroform hydrate and  $-0.75^{\circ}\text{C}$  for carbon tetrachloride hydrate.

Microscopic examination by Montgomery (5) of hydrate crystals formed from dye solutions has not shown any evidence that organic dyes are adsorbed on the crystal.

*3. The third component is of type B and is soluble only in the non-aqueous component.*

Williamson (12) found that hydrate formed from mixtures of chloroform and methyl iodide gave decomposition temperatures lying on a smooth curve between the decomposition temperatures of the pure component hydrates when plotted on a mole percent basis. This is the result that would have been expected if the mixed hydrate formed a solid solution.

The conclusion that the mixed hydrates formed a solid solution had been previously advanced by several other authors according to a literature survey by Palmer (6). Accordingly, Palmer selected as a criterion for hydrocarbon-type hydrates the condition that hydrates of mixtures exhibit behavior typical of solid solutions, at least when there is not a great difference between the molecular size of the components of the hydrate-forming mixture.

The qualification of molecular size is necessary because double hydrates having greater stabilities than either of the simple hydrates of the components have been noted; for example, De Forcrand (8) described a double hydrate of hydrogen sulphide and chloroform having a decomposition temperature of  $16^{\circ}\text{C}$  at 1 atmosphere. The existence of this unusually stable hydrate has recently been confirmed at the University of Oklahoma.

Cyclopentane was selected as a reference compound for the study of the decomposition temperatures of mixed hydrates. The decomposition temperature of cyclopentane hydrate,  $7.2^{\circ}\text{C}$ , is the highest of any known hydrate whose parent compound can be handled as a liquid at room temperature. The hydrate also had been found to form readily when seeded with ice. The behavior of hydrate formers, methyl iodide and cyclopentane, and non-hydrate formers, methylcyclopentane and isopentane, were compared when used as third components in the cyclopentane-water system.

**EXPERIMENTAL.** The hydrocarbons used were obtained from the Phillips Petroleum Company. The cyclopentane ( $n_{\text{D}}^{20} = 1.4049$ ), isopentane ( $n_{\text{D}}^{20} = 1.3538$ ), and methylcyclopentane were designated by the manufacturer as "pure grade," or guaranteed minimum purity 99 mole per cent, and the cyclopentane was research grade with a stated purity of 99.85 mole per cent. Methyl iodide obtained from Eastman Kodak Company was washed with 5% sodium thiosulphate in water, washed three times with water, dried over calcium chloride, and distilled through a 36-inch by 1/2-inch Fenske column packed with 1/8-inch glass helices at a reflux ratio of about 6:1. The boiling point was  $41.0\text{--}41.2^{\circ}\text{C}$  at 740.9 mm.;  $n_{\text{D}}^{20} = 1.5293$ . The samples of methyl iodide were stored in the dark over mercury.

Mixtures of cyclopentane and another compound were made up by weight. About 0.10 to 0.14 moles of the mixture was added to about 300 gm. (17 moles) of ice and water in a pint Dewar flask, and stirred with a Lightnin' Model V

or Model L stirrer. The temperature remained near 0°C until the hydrate was made and the ice melted (a period of from one to two hours). The temperature was observed at one minute intervals until the heating curve indicated that the hydrate was decomposed. Temperature was measured with a seven junction copper-constantan thermocouple.

The heating curves for cyclopentane-cyclopentene mixtures are shown in Fig. 3. Heating curves for the other mixtures were similar in form. The

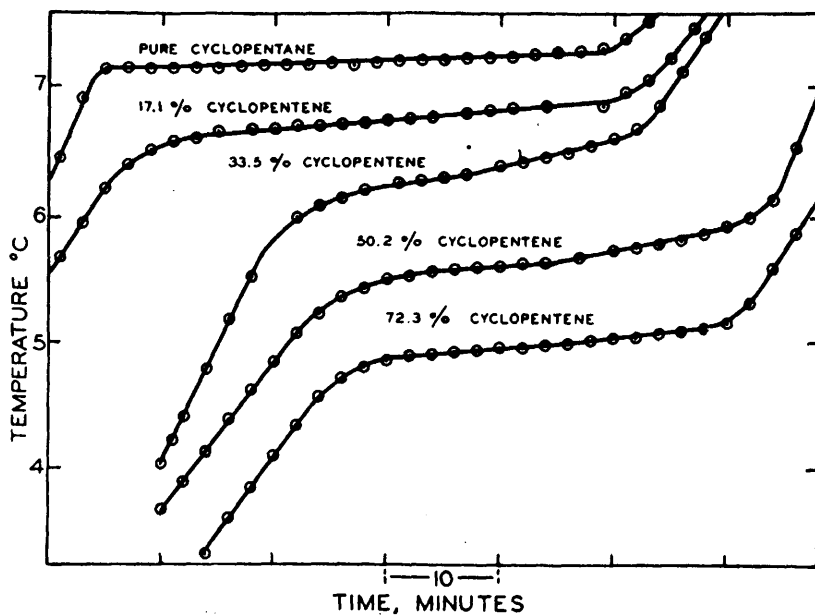


FIGURE 3. Cyclopentane-Cyclopentene Heating Curves

temperature ranges of the plateaus of mixed hydrates were usually greater than those of simple hydrates.

The results are summarized in Table III and shown graphically in Fig. 4. In Fig. 4 the temperature range observed during hydrate decomposition is indicated by a line at the composition of the non-aqueous phase.

The data are in general accord with previous investigations. In the cases of methyl iodide and cyclopentane all mixtures formed hydrates having decomposition temperatures intermediate between those of the hydrates of the components, as was found by Williamson for the mixtures he tested (12). In the case of isopentane and methylcyclopentane which are non-hydrates formers depressions of the decomposition temperatures of cyclopentane hydrate, as indicated by the final plateau temperatures, are seen to be proportional to the mole fraction added component, which is nearly proportional to the molality at these concentrations. Substances soluble in cyclopentane but not in water, and not forming hydrates, lower the decomposition temperature of cyclopentane hydrate about 0.05° per mole percent added substance.

The long plateau ranges observed in the mixtures with isopentane and methylcyclopentane are probably due to the greater concentration of the added component in relation to cyclopentane at the beginning of the decomposition than at the end, due to the release of cyclopentane from the

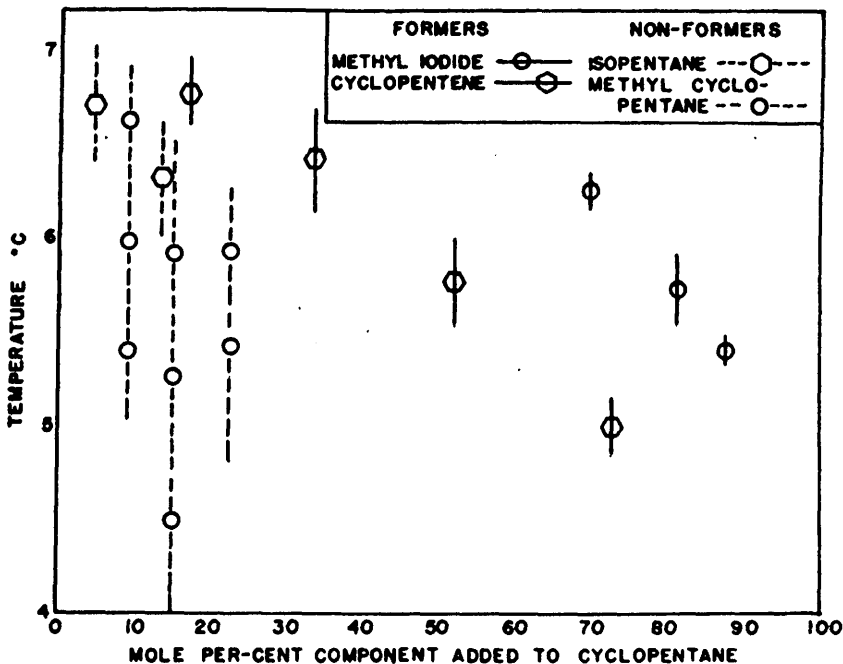


FIGURE 4. Decomposition Temperature Range for Three-component Hydrate Systems

TABLE III

	MOLE % ADDED COMPONENT	PLATEAU TEMPERATURE	
		INITIAL	FINAL
Cyclopentene	17.1	6.60°C	6.95°C
	33.5	6.13	6.67
	50.2	5.52	5.98
	72.3	4.83	5.13
Isopentane	4.85	6.4	7.1
	13.6	6.0	6.6
	50.8	Uncertain, about 2-4°	
Methylcyclopentane	9.05	5.1	6.9
	14.9	?	6.5
	22.5	4.8	6.25
Methyl Iodide	66.4	6.14	6.33
	80.1	5.52	5.90
	87.4	5.32	5.47

hydrate during decomposition. The ranges in cases of mixed hydrates may be influenced also by changes in composition caused by material loss due to evaporation and liquid forced out between the stopper and the flask by the stirrer.

The possibility of change in composition during an experiment was investigated for two of the methyl iodide mixtures by measurement of the refractive index before and after the experiment. The data in Table IV were obtained.

TABLE IV

	REFRACTIVE INDEX	MOLE % CH <sub>2</sub> I
Run 2 initial	1.4890	80.98
final	1.4872	79.3
Run 3 initial	1.4726	69.40
final	1.4650	64.0

CONCLUSIONS. While the foregoing do not provide sufficient basis for a general theory of hydrates formed from mixtures they are in accord with the idea that molecular size is the dominant factor in determining the properties of hydrates of mixtures. It can be anticipated that when both components have molecules of the size that form hydrates of the formula  $M \cdot 16H_2O$ , solid solutions indicated by intermediate decomposition temperatures will be formed by the mixtures of them. When one molecule is too large to form a hydrate itself, and the other is of the size which forms hexadecahydrates, typical depression of the decomposition temperature of the hydrate is observed. The double hydrates can be expected, then, only when one molecule

is rather large (van der Waals diameter perhaps 5.5 Å to 7.0 Å), and the other is small (such as hydrogen sulfide). These data indicate, at least tentatively, that depression of the decomposition temperature of cyclopentane hydrate can be used as a test for hydrate formation, with non-formers showing a uniform depression of 0.05°C per mole percent added component, and formers exhibiting less depression, or possibly an elevation.

4. *The third component is of type C and is soluble in both aqueous and non-aqueous components.*

Maass and Boomer (4) reported the existence of an unexplained hydrate of ethylene oxide containing 6 or more molecules of water and having a melting point of 10.7°C. While ethylene oxide has too much affinity for water to be expected to form a hydrocarbon-type hydrate, it was deemed to be of interest to check the decomposition temperature of the hydrate formed from a mixture of ethylene oxide and chloroform.

A hydrate sample was prepared from 278 gm. of ice, 24 ml. of chloroform and 11 ml. of ethylene oxide. When the ice disappeared, the temperature rose to about -0.7°C, which was taken to be the decomposition plateau. An additional 4 ml. of ethylene oxide was added and the equilibrium temperature dropped to about -1.1°C. Stirring was discontinued for 95 minutes; when recommenced, the hydrate sample had almost disappeared and the temperature rose rapidly from about -0.35°C. This behavior is shown in Table V and Fig. 5.

Since the normal decomposition temperature of chloroform hydrate is 1.7°C, the ethylene oxide had caused a depression.

A further test was made by adding 16 ml. of ethylene oxide to 278 gm. of shaved ice. This mixture was probably on the ice side of the eutectic between ethylene oxide hydrate and ice, hence no hydrate was present at the initial equilibrium temperature of -2.08°C. On adding cold washed chloroform in 5 ml. increments a marked rise in temperature was obtained after the second addition. This was attributed to heat evolved by the formation of chloroform hydrate. Continued addition of cold chloroform soon caused a gradual rise in temperature as the ethylene oxide was diluted. This is shown in Table VI and Fig. 6.

TABLE V

*Time-temperature Values for the System  
Chloroform-Ethylene oxide-Water*

TIME	C	TIME	C
5	-1.95	125	-1.13
10	-1.96	130	-1.09
15	-1.93	-	-
20	-1.89	225	-0.72
25	-1.87	230	-0.70
30	-1.90	235	-0.87
35	-1.85	240	-
40	-1.75	245	-0.63
45	-1.74	250	-0.59
50	-1.68	255	-0.55
55	-1.64	260	-
60	-1.54	265	-
65	-1.55	270	-0.47
70	-1.51	275	-
75	-1.49	280	-0.41
80	-1.42	285	-0.37
85	-1.33	290	-
90	-0.95	295	-
95	-0.73	300	0.28
100	-0.70	305	0.58
105	-0.68	310	1.42
110	-0.68	315	2.10
115 <sup>a</sup>	-0.96	320	2.90
120	-1.12	-	-

<sup>a</sup>4 ml. ethylene oxide added.

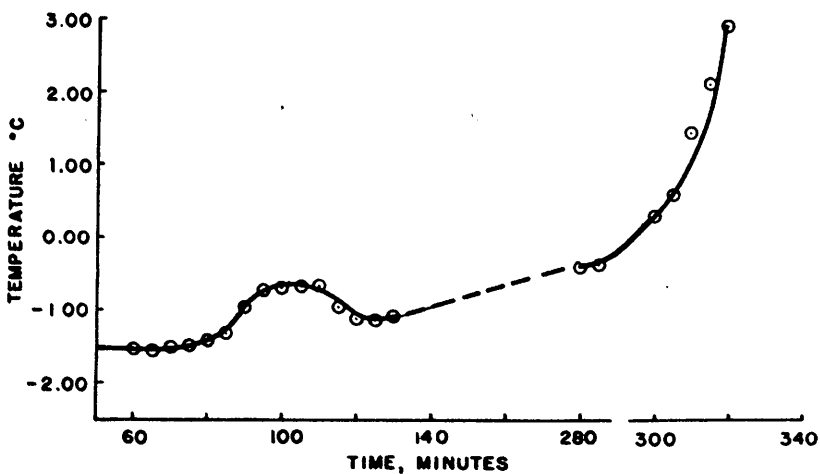


FIGURE 5. Heating Curve for Chloroform Hydrate with Added Ethylene Oxide



TABLE VI  
Amount of Chloroform  
Added to the Chloroform-Ethylene oxide-Water System  
with Resulting Equilibrium Temperatures.

ML.	CHLOROFORM ADDED MOLE	MOLE %	TEMPERATURE °C
0	0.0	0	-2.08
5	0.063	16	-2.06
10	0.13	28	-1.98
15	0.19	37	-1.10
20	0.25	43	-1.16
25	0.32	49	-1.11
30	0.38	54	-0.94
35	0.44	57	-0.75
40	0.50	60	-0.56
45	0.57	63	-0.44
50	0.63	66	-0.34
55	0.69	68	-0.23
60	0.76	70	-0.13
65	0.82	71	-0.04
70	0.88	73	0.03
75	0.95	74	0.11
-	-	100	1.72 <sup>a</sup>
-	-	48	-1.10 <sup>b</sup>
-	-	58	-0.68 <sup>b</sup>

<sup>a</sup>Decomposition temperature of chloroform hydrate

<sup>b</sup>Values taken from Table 6 of this paper

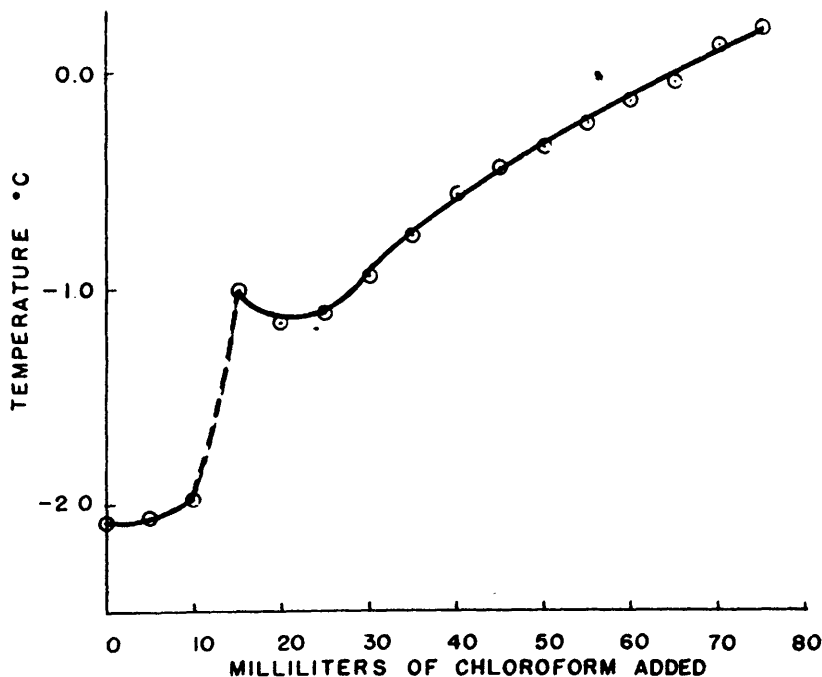


FIGURE 6. Addition of Chloroform to Ethylene Oxide-Water Mixture

The evidence indicates that ethylene oxide does not form a hydrate of the same type as chloroform hydrate. From the standpoint of chemical microscopy, however, no distinction is discernible, and ethylene oxide hydrate is of the hydrocarbon type.

*5. The third component is an indifferent gas such as air.*

Slater (8) and other workers at the University of Oklahoma noted that marked evolution of gas results from decomposing hydrate crystals. This led Slater to investigate the consumption of air during hydrate formation; and the subsequent release on decomposition. He found that at atmospheric pressure more than a liter of gas was used per mole of chloroform or carbon tetrachloride hydrate formed. With carbon dioxide (a hydrate former at high pressures) more than 4 liters were consumed at atmospheric pressure. With hydrogen (considered too small to form hydrate) only a third of a liter was consumed. The amount of air consumed was not affected by a 10% variation in pressure, contrary to what might have been expected for a case of simple adsorption.

Sampson (7) found it necessary to repeat a large portion of his hydrate vapor pressure measurements because the samples had been prepared in air at atmospheric pressure; with samples prepared in a vacuum, the vapor pressures were a few tenths of a millimeter lower.

The inclusion of air has been noted by von Stackelberg (9). There is undoubtedly a relation with effects described by Villiard (10) who found that indifferent gases at high pressures greatly increased the thermal stability of hydrates formed from liquids. Mechanical pressure was without effect, but hydrates such as that of carbon disulphide are stable only under high pressure of indifferent gases.

*6. Removal of third components by fractional crystallization using hydrate formation.*

Williamson (12) reported failure in preliminary attempts to separate benzene from chloroform, or ethyl iodide from methyl iodide, by hydrate formation. He did not pursue the question further.

More recent trials, using alpha bromonaphthalene as an index impurity which could be easily analyzed by refractive index measurements, showed positive results. Hydrate from a 200% excess of chloroform containing 10% by weight impurity was drained and washed 3 times with water, decomposing about one-third of the sample with each wash. Chloroform recovered from the final wash contained only 5% impurity. The same degree of purification could be effected in one step by preparing hydrate in the same way, squeezing out the adhering impure mother liquor mechanically, and recovering the partially purified chloroform by decomposing the squeezed hydrate.

Still more recent results from other workers in this laboratory indicate that the best commercially available grades of nitromethane can be further purified through hydrate formation.

In each case the efficiency of the purification depends on the method used for separating the mush of finely divided hydrate crystals from the supernatant liquid in which the impurity is concentrated.

*7. The third component is an isotopic variety of water.*

This is a special case of interest in connection with the problem of fractionating heavy water. Heavy water forms hydrogen bonds that are stronger and longer than in ordinary water, hence it might be expected to make larger and stronger cages around the molecule that forms the hydrocarbon-type hydrate. No conclusive studies have been made on this point, although Godchot, Caiquill, and Calas (2) reported that rough measurements on the

deuteriohydrate of krypton and xenon showed a very close resemblance to the corresponding hydrate as far as vapor pressures are concerned. It is possible that with hydrates of less volatile materials, the slight difference between hydrogen and deuterium bonds could be greatly exaggerated when manifested in terms of hydrate stability or some other hydrate property.

#### BIBLIOGRAPHY

1. FORCRAND, R. DE, 1883. Recherches sur les hydrates sulphydres. *Ann. chim. et phys.*, 5th Series, 28: 5-67.
  2. GODCHOT, M., CARQUIL, G., AND CALOR, R., 1936. Deuteriohydrates of krypton and xenon. *Compt. rend.*, 202: 759-760.
  3. LIPPERT, E. L. 1949. Effect of alcohols on the decomposition temperature of chloroform hydrate. *Proc. Oklahoma Acad. Sci.* 30 : 221-225.
  4. MAASS, O. and BOOMER, E. H., 1922. The properties of ethylene oxide compound to oxygen compounds of similar molecular weight. *J. Am. Chem. Soc.*, 44: 1720.
  5. MONTGOMERY, D. P., 1951. Unpublished Thesis. University of Oklahoma, Norman, Oklahoma. (In preparation).
  6. PALMER, H. A., 1950. Unpublished Thesis. University of Oklahoma, Norman, Oklahoma.
  7. SAMPSON, J. A., 1948. Unpublished Thesis. University of Oklahoma, Norman, Oklahoma.
  8. SLATER, J. D., 1950. Unpublished Thesis. University of Oklahoma, Norman, Oklahoma.
  9. STACKELBERG, V. VON, 1949. Feste Gashydrates. *Naturwissenschaften* 36: 327-33, 359-62.
  10. VILLARD, P., 1897. Etude experimentale des hydrates de gaz. 7th Series 11: 289-394.
  11. WHALEN, J. W., 1951. Unpublished Thesis. University of Oklahoma, Norman, Oklahoma.
  12. WILLIAMSON, V. D., 1948. Unpublished Thesis. University of Oklahoma, Norman, Oklahoma.
-